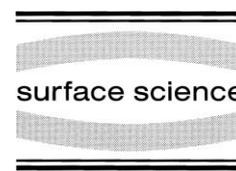




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X-ray excitation of DX centers in Si-doped $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$

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Abstract

We report on the use of X-rays to excite DX centers in Si doped $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ into their shallow donor state, as monitored by measuring the resulting persistent photoconductivity. The energy dependence of the photoconductivity closely follows the simultaneously detected X-ray fluorescence, indicating that photoexcitation of core holes is an efficient primary excitation step for the excitation of DX centers. However, there is no appreciable difference between the Ga and As K-edges, implying a non-local DX center excitation mechanism. © 2000 Elsevier Science B.V. All rights reserved.

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Si dopants in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ act as deep donor levels (DX centers) when $x > 0.22$ [1–3]. These DX centers can be photoexcited to a metastable state in which they are shallow donors. In analogy to DIET (desorption induced by electronic transitions) processes at surfaces, the excitation process involves atomic motion on an excited-state potential energy surface, resulting in a drastic atomic rearrangement in the bulk. In addition to the structural change, two electrons are injected into the conduction band in the process, increasing the conductivity [4]. This effect has been studied extensively using visible light in bulk materials [5–7] and also in heterostructures [8–10]. In this work, we present for the first time

the use of X-rays to induce photoconductivity in $\text{Al}_x\text{Ga}_{1-x}\text{As}$: Si.

The sample that we studied was $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ doped with Si, which was obtained from Quantum Epitaxial Design. All the layers of the sample were grown using molecular beam epitaxy. On a semi-insulating GaAs substrate, a 200 nm thick GaAs buffer layer was grown, followed by a 1.5 μm thick layer of $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ and a 1 μm thick Si-doped $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ layer, which was capped with a 10 nm thick GaAs layer. Previous studies of such samples using visible light have demonstrated persistent photoconductivity and a doping concentration of $N_\infty \sim 5 \times 10^{19} \text{ cm}^{-3}$, which was deduced from the infinite-temperature extrapolation of the carrier density measured using the Hall effect [11]. This is a factor of 50 larger than the nominal value

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of $N_d \sim 1.0 \times 10^{18} \text{ cm}^{-3}$ quoted by the manufacturer. The sample geometry was a 6 mm \times 2 mm rectangular wafer with two ohmic contacts separated by 4 mm. Two-terminal conductance measurements were performed using a lock-in technique with an excitation voltage of 33 mV. The X-ray beam spot size at the sample was about 1 mm in diameter and was centered between the two ohmic contacts.

As the sample is cooled in the dark, the thermal equilibrium conductance decreases due to the Boltzmann distribution of donors in the excited (shallow donor) state and the ground state (DX level). In the process of a donor switching from the metastable state to the ground state, two electrons in the conduction band become trapped at the DX center, resulting in a decrease in carrier density. In order to study the effect of X-rays on the conductivity, we cooled the sample in the dark to 120 K and measured the time-dependent photoconductance as a function of X-ray beam flux. This temperature is slightly above the annealing temperature (~ 100 K) [1], which is the temperature above which the photoconductivity ceases to be persistent. Fig. 1 shows the time-dependent photoconductance together with the fluorescence yield as the X-ray beam is switched on and off. In the case of the fluorescence yield, the response to the X-ray beam is instantaneous since there is no metastable state in the process. In contrast, the photoconductance exhibits a delayed response. As the X-ray beam is turned on, the conductance rises from the thermal equilibrium value and reaches a steady state within a few minutes. On a similar time scale, it decays back to the thermal equilibrium value when the X-ray beam is switched off. This non-equilibrium steady state value is reached when the excitation rate to the shallow donor state is equal to the decay rate to the ground state. The excitation rate consists of two terms (excitation due to the X-ray beam and due to thermal excitation), whereas the decay rate is governed only by a thermal process.

The rate equation for the number of donors in the excited state is given by

$$\frac{dN_{\text{ex}}}{dt} = AIN_g + B(e^{-\beta E_e} N_g - e^{-\beta E_c} N_{\text{ex}}), \quad (1)$$

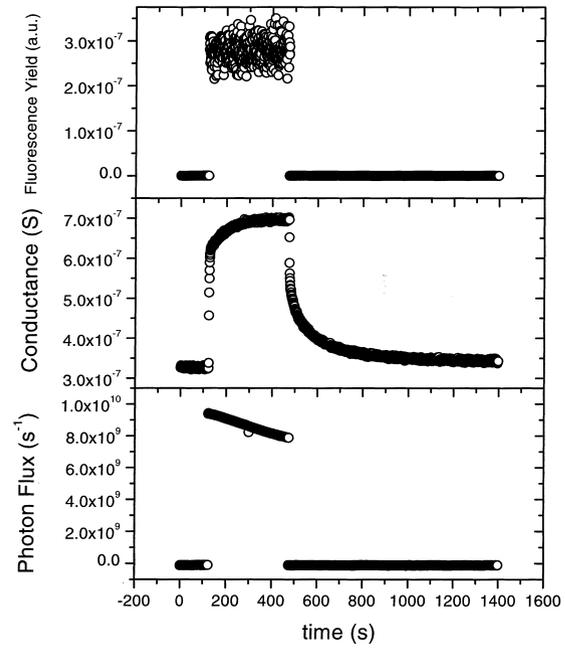


Fig. 1. Time-dependent effect of X-rays on the photoconductance. The beam intensity was monitored along with the fluorescence and the conductance. As the beam is switched on, the fluorescence yield jumps to a finite value instantaneously, whereas the photoconductance rises with a time constant to a steady-state value. As the beam was switched off, the fluorescence yield vanishes immediately, whereas the photoconductance decays with a time delay. This illustrates the difference in the fluorescence and photoconductance process, where a metastable state is involved in the latter.

where N_{ex} is the number of donors in the excited state, N_g is the number of donors in the ground state, A and B are proportionality constants, I is the incident photon flux, $\beta \equiv 1/kT$, and E_e and E_c are the emission barrier and the capture barrier, respectively. E_e and E_c for Si-doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ at $x=0.35$ are 0.43 and 0.21 eV, respectively [12–14]. The steady-state population of donors in the excited state obtained by setting Eq. (1) to zero is

$$N_{\text{ex}} = \frac{AI + Be^{-\beta E_e}}{AI + B(e^{-\beta E_e} + e^{-\beta E_c})} N_d. \quad (2)$$

Here, we substituted $N_g = N_d - N_{\text{ex}}$, where N_d is the total number of dopants. In the limit where there is no X-ray excitation ($I=0$), we recover the Boltzmann distribution. At zero temperature (with $I>0$), the steady state is achieved when all the

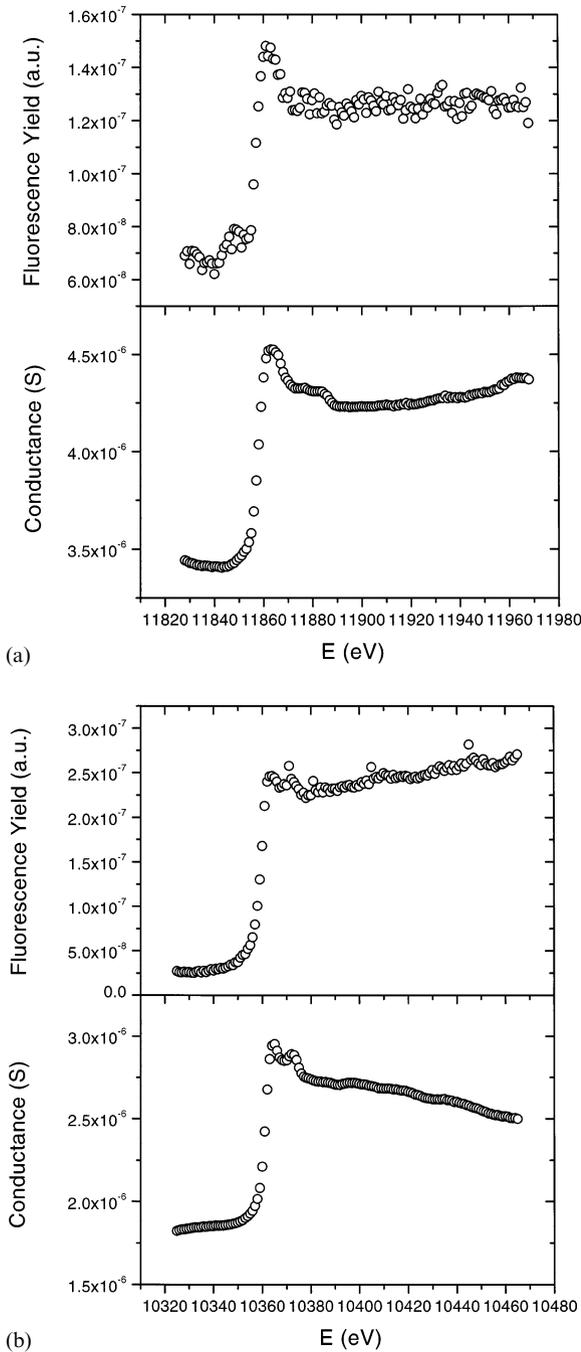


Fig. 2. K-edge scan of the photoconductance together with the fluorescence yield for As (a) and Ga (b). For both K-edge scans, the photoconductance closely follows the fluorescence yield curve, indicating that the core-hole excitation is a primary step for the excitation of *DX* centers. The step size in the photoconductance edge normalized by the X-ray beam flux is $3.7 \times$

donors have been excited to the shallow donor state. If we define $\Delta N_{\text{ex}} = N_{\text{ex}}(I) - N_{\text{ex}}(I=0)$ to refer to the excess number of donors in the excited state from the thermal equilibrium value, Eq. (2) leads to

$$\Delta N_{\text{ex}} = \frac{AI}{\{AI + B(e^{-\beta E_e} + e^{-\beta E_c})\}(1 + e^{-\beta E_b})} N_d, \quad (3)$$

where $E_b = E_e - E_c$ is the *DX* center binding energy. According to this expression, the higher the temperature, the smaller the number of excess donors in the excited state from the thermal equilibrium value due to X-ray excitation. This consequently gives a shorter time constant to reach that steady-state value. This is consistent with our measurements done at a higher temperature $T = 150$ K. At this temperature, the photoconductance had a smaller value than that at 120 K, and the time constant was smaller.

An important issue is to determine the efficiency of the generation of photocarriers as a function of X-ray energy. At 120 K, we compared As K-edge with Ga K-edge excitation. While scanning the incident beam energy, we monitored the fluorescence yield and the photoconductance simultaneously. Since the photoconductance is a non-equilibrium effect, which has a finite time constant to reach the steady state, it is crucial to allow a sufficient successive time between each data point when scanning the energy. We chose a settling time of 11 and 10 s for the As and Ga K-edge scan, respectively. The results are plotted in Fig. 2. The first notable observation is that for both K-edge scans, the photoconductance has the same edge profile as the fluorescence yield. The second notable observation is that the height of the step at the edge, normalized by the incident photon flux,

10^{-17} S/photon and 3.0×10^{-17} S/photon for the As and the Ga K-edge, respectively. The similarity in the step height between the two K-edges suggests that the excitation mechanism of the *DX* centers is non-local. The apparent small pre-edge feature in the As fluorescence data is a manifestation of the limited signal-to-noise ratio. It is not reproducible in repeated scans.

is very similar for the As (3.7×10^{-17} S/photon) and Ga (3.0×10^{-17} S/photon) K-edges.

These results have several implications. First, they indicate that core-hole excitation is an efficient primary step for the excitation of *DX* centers. Second, they indicate that the *DX* center excitation mechanism is non-local. If the *DX* center excitation mechanism were local (such that only the four As neighbour atoms of the Si atom would contribute to the transformation of the *DX* centers to shallow donors when excited by the X-ray photon), then we would not expect to see an edge in the photoconductance at the Ga K-edge. In addition, the location of the photoconductance edge would likely differ from that of the fluorescence yield, since the electronic structure of the As atoms involved in the *DX* centers is expected to be different from the majority of As atoms. The fact that we see an edge in the photoconductance at the Ga K-edge, which has the same step height as the As K-edge, and that the locations of the edges for the photoconductance coincide with those for the fluorescence suggests that core-hole excitations of As and Ga atoms not directly bonded to the *DX* centers can excite the *DX* centers. Once a core hole is excited, it is followed by a chain of Auger decay and fluorescence processes, which result in a cascade of energetic photons, electrons, and holes. The photons can be reabsorbed after propagating large distances and create more electrons and holes. Eventually, these carriers relax and become thermalized band-edge carriers (and excitons) that, due to their long lifetime, have the potential to diffuse over large distances. In this way, they can excite *DX* centers far from the core hole excitation site. The mechanism for this excitation likely involves band-edge holes recombining with the negatively charged *DX* centers, which then become unstable towards transformation to the shallow donor state and, upon structural relaxation, emit another electron [4].

Recently, Ishii et al. have claimed that the local structure of the *DX* center can be detected by monitoring the change in capacitance induced by X-ray excitation and the fluorescence simultaneously [15]. A small shift (<2.5 eV) in the location of the edge in the capacitance measurement with respect to the edge in the fluorescence was

observed, which was attributed to the selective observation of the local structure of the *DX* centers. For high scale speeds, we also observed such a shift in our photoconductance measurements. However this shift disappeared if the scan speed was reduced to allow the photoconductance to reach a steady state at each data point. Therefore, our observed shift at high scan speeds is an artifact due to the slow time response of the photoconductance.

After identifying the efficient excitation path, we proceeded to cool the sample in order to induce persistent photoconductivity. The sample was cooled to 10 K, at which temperature the sample was insulating with a conductance of 2.0×10^{-8} S. We exposed the sample to an X-ray beam with a photon energy of 10 367 eV (2 eV above the Ga K-edge) and 11 865 eV (2 eV above the As K-edge). The results for both core-hole excitations were similar. In Fig. 3, we plotted the result for

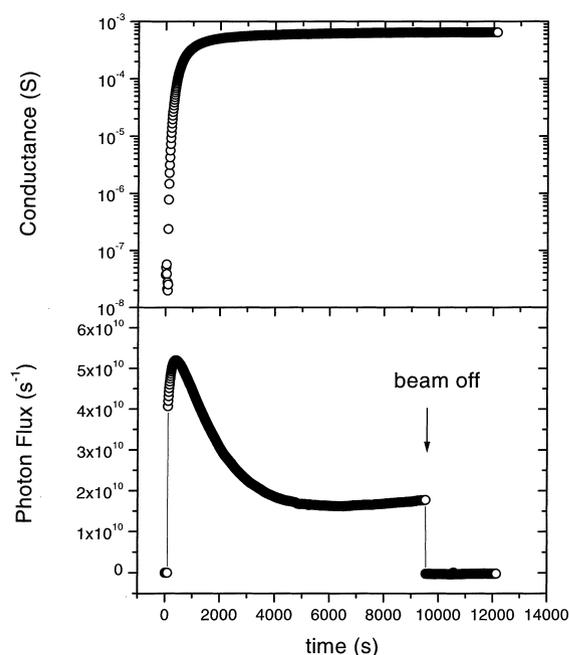


Fig. 3. Persistent photoconductance at 10 K induced with an X-ray beam energy of 10 367 eV (2 eV above the Ga K-edge). The conductance saturated to 6.2×10^{-4} S after an hour of X-ray exposure, higher than the thermal equilibrium conductance of 2.2×10^{-4} S at 300 K. After the beam was turned off, the photoconductance persisted.

the Ga K-edge excitation. As the beam was turned on, the conductance rose sharply and saturated after roughly an hour of X-ray beam exposure. The saturation value of the conductance was 6.2×10^{-4} S, higher than the thermal equilibrium conductance of 2.2×10^{-4} S at 300 K. Such a high conductance can be considered metallic. Upon turning off the beam, the conductance persisted during the time that we monitored, which was 8 h.

The fact that a 1 mm beam can convert the whole sample (4 mm distance between the leads) to a metallic conductor suggests that the extent of the non-locality is at least of the order of several millimeters. At present, we do not understand the origin of this apparent macroscopic non-locality. In particular, we have not excluded the possibility that the beam may spill beyond the nominal 1 mm diameter X-ray spot size. We can calculate the quantum yield, Q , for the DX center excitation from the initial slope of the time-dependent conductance in Fig. 3. Assuming that at the saturation level, all the donors would have been converted into shallow donors, Q is given by

$$Q = \frac{dG/dt N_d}{2G_{\text{sat}}I}, \quad (4)$$

where G represents the conductance, dG/dt is the initial slope of the conductance, and G_{sat} is the saturation value of the conductance. The factor of 1/2 is due to the fact that in the ground state, only half of the dopants are in the DX configuration due to charge neutrality constraints. The total number of dopants in the sample volume is approximately $N_d \sim 5 \times 10^{14}$ (or 1×10^{13} if we use the manufacturer's nominal value for the dopant concentration). By applying this value and the measured initial slope of the conductance of 1.7×10^{-6} S/s, $G_{\text{sat}} = 6.2 \times 10^{-4}$ S, and $I = 4.5 \times 10^{10}$ photons/s into Eq. (4), we obtain a quantum yield of 12 (or 0.24 using the nominal dopant concentration). To obtain a more accurate value for the quantum yield, it would be necessary to measure the carrier concentration at the saturation level using the Hall effect.

To summarize, we studied DX center excitation using X-rays as the excitation source. Our results show that the excitation mechanism is non-local. The large penetration depth of the X-rays compared to visible light has potential applications in inducing metallic behavior at layers buried deep beneath the surface.

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